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Unexpected reversible pyrazine based methylation in a Ru(II) complex bearing a pyrazin-2′-yl-1,2,4-triazolato ligand and its effect on acid/base and photophysical properties†‡

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The regioselective methylation of a ruthenium polypyridyl complex bearing both a 1,2,4-triazolato and a pyrazine moiety is reported. In contrast to previous studies in which methylation of the 1,2,4-triazolato ring was observed, in the present system methylation takes place exclusively at the non-coordinated nitrogen of the pyrazine ring. The monomethylation is confirmed by ^{1}H NMR spectroscopy and ESI-MS and the electronic properties of the methylated complexes are studied by UV/vis absorption, emission, surface enhanced, resonance and transient resonance Raman spectroscopy. Ligand deuteriation is used to simplify the ^{1}H NMR spectra and to assign definitively the Raman spectra. Acid–base studies show that the triazolato ring of the *N*-methylated complexes can be protonated at low pH and that at high pH the *N*-methyl group can be deprotonated reversibly. Furthermore it is shown that under conditions where the methyl group is deprotonated, demethylation occurs to recover the initial complex.

Introduction

Transition metal complexes, many containing polypyridyl ligands, have seen extensive application in the development of molecular devices including solar cells, sensors, and photocatalysts.[1] An essential aspect in controlling the properties of such systems requires the development of synthetic methods that allow for manipulation of their structural and electronic properties. Direct reaction between ligands and metal ions is the conventional method to prepare metal complexes. However, the synthetic modification of ligands *post complexation* has seen increasing application. Examples of this approach in the synthesis of Ru(II)polypyridyl complexes are the use of coupling reactions to prepare well defined multinuclear assemblies such as those reported by the groups of Tor[2], Hanan[3] and Vos[4] and the modification of coordinated ligands[5] for example methylation of complexes as shown by Campagana, Balzani,[6] Vos[7] and co-workers. In the former case the use of methylation as a protecting group strategy was employed in the synthesis of complex multinuclear assemblies.[8] Typically, however, complexes in which only a single site is available for modification by methylation are employed; due to the use of reactive and hence potentially non-selective reagents, such as $(CH_3)_3OBF_4$.

Pyrazine based ligands have attracted much attention in the last number of years in coordination chemistry, both because of pyrazine's potential to act as a bridging ligand in multinuclear complexes and its tuneable π-acceptor properties, through the non-coordinated nitrogen atom.[9] As such the pyrazine moiety has been used extensively in multinuclear assemblies in particular to manipulate the excited state properties of the compounds and to investigate and promote the intercomponent interaction between different molecular components.[10] One of the best known and much studied compounds is the Creutz–Taube ion,[11] a species that initiated the investigation of the electronic communication between metal centres *via* a connecting bridge.[12,13] These studies show that in multinuclear systems the pyrazine based π* level is stabilised upon binding of a second metal centre. In our group, the relatively good π-acceptor ability of pyrazine has been combined with

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†Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.
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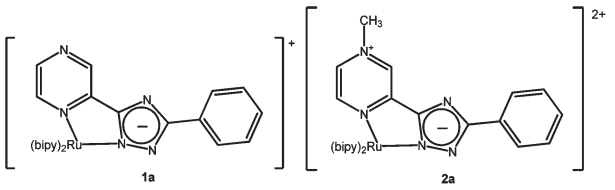

Fig. 1 Molecular structure of complexes **1a** and **2a**.

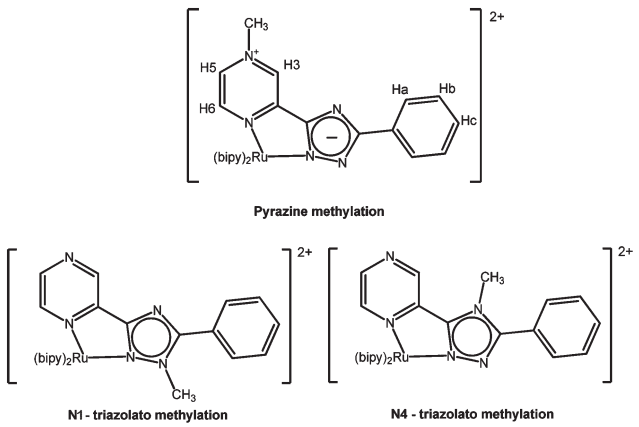

Fig. 2 Possible structural isomers, which can be formed following methylation of **1a**.

the strong σ-donor/weak π-acceptor 1,2,4-triazole moiety.[14] These ligands, containing both a good σ-donor and a good π-acceptor moiety, form Ru(II)polypyridyl complexes in which the photophysical, photochemical and electrochemical properties are strongly dependent on the protonation state of the triazole ring or, *albeit* less studied, of the pyrazine ring. For example, the complexes are photostable when the triazole ring is deprotonated and photochemically active when protonated.[15] In the case of a pyrazine bridged binuclear complex bearing two 1,2,4-triazole units the reverse was observed with the deprotonated complex being photochemically active.[16]

Here we report an unexpected selectivity for methylation of pyrazine nitrogens of **1a** ($[Ru(bipy)_2(phpztr)]PF_6$ where phpztr$^-$ = 3-pyraz-2′-yl-5-phenyl-1,2,4-triazolato) to form **2a** ($[Ru(bipy)_2(Mephpztr)](PF_6)_2$ (Fig. 1) over, in principle, more nucleophilic 1,2,4-triazole nitrogens in a heteroleptic Ru(II)polypyridyl complex (Fig. 2). The synthesis, characterisation and the effect of quaternisation of the pyrazine ring nitrogen on the spectroscopic and acid–base properties of (**2a**), together with selectively deuteriated analogues (**2b**, **2c**) to facilitate characterisation, are reported. Furthermore we show that subsequent demethylation can proceed under mild conditions making the approach useful in building well defined multinuclear complexes.[6]

Results and discussion

Synthesis and characterisation

1a was prepared following a literature method previously reported and was isolated as the N2 bound isomer (Fig. 1).[14]

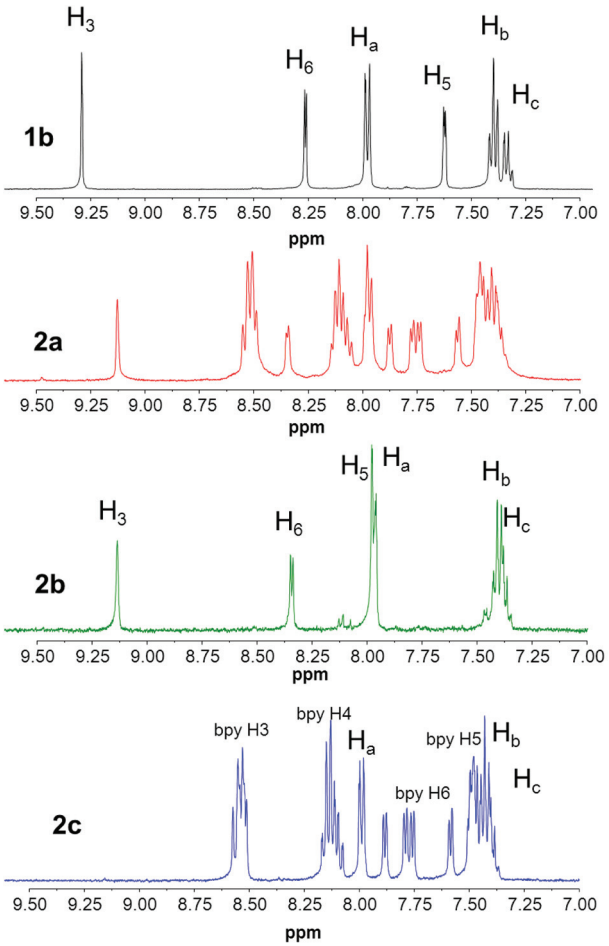

Fig. 3 ^{1}H NMR spectra (7–9.5 ppm) of **1b**, **2a**, **2b** and **2c** in CD_3CN.

$[D_8]$-bipy and $[D_3]$-Hphpztr (in which the pyrazine hydrogens have been exchanged)[17] were used to aid in analysis of ^{1}H NMR and Raman spectra. Methylation was carried out quantitatively by reaction of **1a–c** with $(CH_3)_3OBF_4$ in acetonitrile, which yielded a purple product, and not an orange compound as reported earlier for related $[Ru(bipy)_2L]^+$ complexes (where L = pyridine or pyrazine-1,2,4-triazole type ligands).[7]

The methylated complex $[Ru(bipy)_2(Mephpztr)]^{2+}$ **2a** and the deuteriated analogues $[Ru([D_8]\text{-bipy})_2(Mephpztr)]^{2+}$ **2b** and $[Ru([H_8]\text{-bipy})_2([D_3]\text{-Mephpztr})]^{2+}$ **2c** are dicationic as confirmed by ESI-MS. The ^{1}H NMR spectra of the complexes **1b** and **2a–2c** are shown in Fig. 3. Spectra were assigned using ^{1}H COSY NMR spectroscopy and facilitated by the availability of the isotopologues **2b** and **2c**. Methylation of compound **1a** led to relatively minor changes in the aromatic region of the spectrum. For **2a** a full set of the expected aromatic signals and a single resonance at 4.25 ppm, assigned to the *N*-CH_3 group were observed.

For complex **1a**, there are three possible sites for methylation; the non-coordinated nitrogen atom of the pyrazine ring or the N_1 or N_4 nitrogen atoms of the 1,2,4-triazolato ring (Fig. 2). ^{1}H NMR spectroscopy of related methylated complexes, such as $[Ru(bipy)_2(pytr)]^+$ and $[Ru(bipy)_2(pztr)]^+$ (where

Hpytr is 3-(pyridin-2′-yl)-1,2,4-triazole, and Hpztr is 3-(pyrazin-2′-yl)-1,2,4-triazole), have shown the formation of both the N_1-Me and the N_4-Me isomers in the ratio of 70 : 30, where the 1,2,4-triazolato ring is methylated.[7] Hence, it was expected that **1a** would undergo methylation of the 1,2,4-triazolato ring also. It is apparent from elemental analysis and mass spectrometry that complexes **2a–c** are methylated at a single position, which is confirmed by ^{1}H NMR spectral data.

The methyl group of the N_1-Me isomer $[Ru(bipy)_2(1\text{-Mepztr})]^{2+}$ were reported to be at 3.17 ppm, whereas that of the N_4-Me analogue was at 4.26 ppm.[7] For **2a–c** the methyl hydrogens was observed at 4.25 ppm indicating that methylation occurs at the N_4-position of the 1,2,4-triazolato ring. However, the purple colour of the complexes (*vide infra*) suggests that this is not the case as *N*-methylated 1,2,4-triazole based complexes of this type are typically orange.[7,18,19] Furthermore, the chemical shifts for the hydrogens of the pyrazine ring were at 9.13 (H_3), 7.97 (H_5) and 8.32 (H_6) ppm for **2a** whereas they were at 9.29 (H_3), 7.60 (H_5) and 8.25 (H_6) ppm for **1a** (Fig. 3). Typically for related complexes where the 1,2,4-triazolato ring was methylated[18] the H_3 resonance was observed between 9.47 and 9.79 ppm and the H_6 resonance at *ca.* 8.60 ppm.

In summary the ^{1}H NMR spectroscopic data indicate that methylation does not occur at the 1,2,4-triazolato ring but instead at the non-coordinated nitrogen of the pyrazine ring in **2a–c**. This conclusion is supported by UV/Vis absorption and Raman spectroscopy (*vide infra*).

Quantum chemical calculations

Molecular orbital calculations were used to establish the atomic composition of the HOMO of both **1a** and the non-phenyl complex, $[Ru(bipy)_2(pztr)]^{2+}$ (where pztr = 3-(pyrazin-2′-yl)-1,2,4-triazolato). The calculations (see ESI‡ for further details) showed that the relative contribution of the pyrazine N atom was approximately three times greater in complex **1a** compared to $[Ru(bipy)_2(pztr)]^{2+}$. As the HOMO of **1a** has a greater contribution of the pyrazine N atom than that of the non-phenylated complex, it is likely that increased nucleophilicity plays a role in the selectivity observed.

Electronic absorption and emission spectroscopy

The UV/Vis absorption spectra of **1a** and **2a** are shown in Fig. 4 and 5. The absorption spectrum of **1a** in its three protonation states, *i.e.* fully deprotonated (**1a**, λ_{max} 450 nm), protonated at the 1,2,4-triazolato ring (H**1a**, λ_{max} 430 nm) and protonated at both the 1,2,4-triazolato and pyrazine rings (H_2**1a** $[Ru(bipy)_2(H_2phpztr)]^{2+}$, λ_{max} 535 nm) are shown in Fig. 4.

The UV/Vis absorption spectrum of **1a** comprises of a broad absorption in the visible region (λ_{max} 450 nm) assigned as an ^{1}MLCT ← GS manifold.[14,20] The intense absorption band at ~285 nm is assigned to a (bipy) ligand centred (π–π^*) transition. Protonation of the 1,2,4-triazole moiety (H**1a**) results in minor changes to the shape of the ^{1}MLCT ← GS absorption band with the λ_{max} shifting to 430 nm, due to the changes protonation induces in the σ-donor/π-acceptor properties of the triazole moiety. Under strongly acidic conditions protonation of the non-coordinated nitrogen of the pyrazine moiety occurs,[18] to form H_2**1a**. Substantial changes are observed in the UV/Vis absorption spectrum with the appearance of an absorption band (λ_{max} 530 nm) assigned earlier to a Ru(II)-pyrazine H^+ based ^{1}MLCT ← GS transitions and at 375 nm assigned to Ru(II)-bipy based ^{1}MLCT ← GS transitions.[21]

The spectrum of **2a** in acetonitrile is shown in Fig. 5 together with the spectra of H**2a** and H_2**1a** in acetonitrile for comparison. In all three cases two strong absorption bands at *ca.* 540 nm and at *ca.* 375 nm are observed indicating that their electronic properties are similar; *i.e.* that the pyrazine is cationic, and hence that the pyrazine is *N*-methylated in the case of **2a**/H**2a**. The small blue shift of both ^{1}MLCT ← GS absorption bands upon protonation of **2a** indicates that it

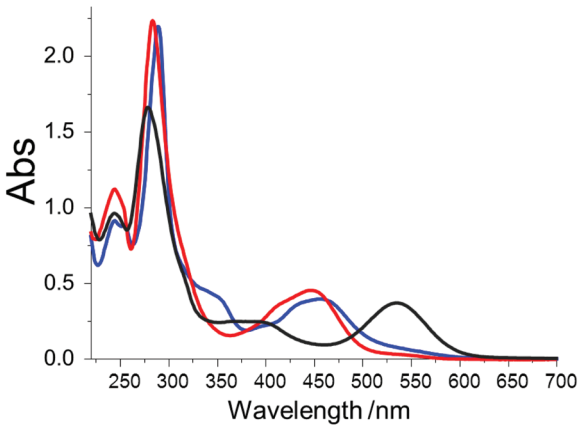

Fig. 4 UV/Vis absorption spectra of **1a** (blue 3.36 × 10^{-5} M), H**1a** (red 3.51 × 10^{-5} M) and H_2**1a** (black 1.06 × 10^{-5} M) in acetonitrile. Triflic acid was added to protonate the complex.

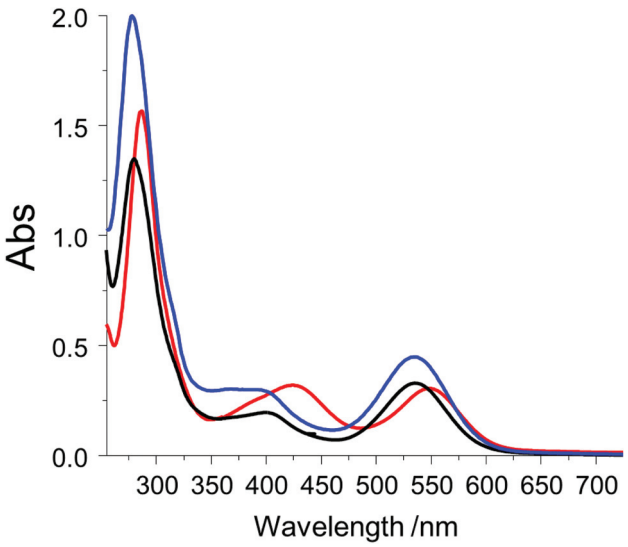

Fig. 5 UV/Vis absorption spectra of **2a** (red 3.50 × 10^{-5} M), H**2a** (black 3.04 × 10^{-5} M) and H_2**1a** (blue 3.85 × 10^{-5} M) in acetonitrile. Triflic acid was added to protonate the complexes.

involves the 1,2,4-triazole moiety in this case. The acid base chemistry of **2a** is discussed further below.

Room temperature emission spectra and lifetime data for **1a** and H**1a** in acetonitrile were reported earlier[21] and were assigned to arise from ^{3}MLCT excited states. As observed for the absorption spectra, the emission maximum (655 nm) of H**1a** is blue shifted compared to **1a** (670 nm). By contrast both **2a** and H**2a** were found to be non-emissive, possibly as a result of a decrease in the energy of the ^{3}MC state due to the reduced σ-donor properties of the (*N*-methylated)pyrazine-1,2,3-triazole ligands compared with the non-methylated ligand. Lowering of the ^{3}MC level removes the thermal barrier to deactivation of the emissive ^{3}MLCT excited states.[22–24] The lack of emission from **2a** further supports the structural assignment made by ^{1}H NMR spectroscopy, as complexes reported earlier in which the 1,2,4-triazolato ring is methylated are emissive.[7,25]

Acid base properties

The acid–base properties of compounds **1a** and **2a** were investigated in Britton–Robinson buffer, in acetonitrile and in H_2SO_4 (aq.). A single protonation step, *i.e.* protonation of the 1,2,4-triazolato moiety, was observed between pH 1 and pH 7 for **1a** (pK_a = 3.1).[26] By contrast the UV/Vis absorption spectrum of **2a** is constant over this pH range and protonation of the triazolato takes place only under highly acidic conditions (*i.e.* <pH 1). Protonation can be achieved in dry organic solvents with strong acids or in conc. H_2SO_4 (aq.). The increased acidity of a 1,2,4-triazolato moiety in **2a** is expected considering the effect, observed previously, of substituents on the triazole ring at the 5 position; for example replacing the phenyl ring in **1a** with a bromine results in a decrease in pK_a to 1.4.[4b,27] By contrast between pH 7 and 12, where **1a** does not show acid base chemistry, for **2a** dramatic changes in the UV/Vis absorption spectrum are observed. Between pH 9 and 11, with a pK_a at 9.9, four isosbestic points are maintained (Fig. 6), which is consistent with deprotonation.

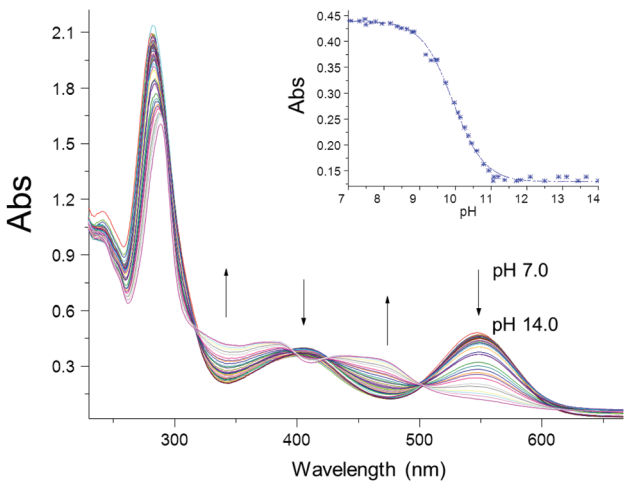

Fig. 6 pH dependence of the absorption spectrum of **2a** (4.50×10^{-5} M) in Britton–Robinson buffer. the pH was adjusted by addition of NaOH or H_2SO_4. Inset shows a plot of intensity *vs.* pH at 550 nm.

As the protonation of the 1,2,4-triazolato ring occurs only under highly acidic conditions the deprotonation at pH 9.9 was tentatively assigned to deprotonation of the *N*-methyl group of the pyrazine ring. Furthermore after short periods (min) at pH 10.5, the original spectra (*i.e.* at pH 1) can be recovered fully by addition of acid (Fig. 7).

At high pH deprotonation of the methyl group is followed by irreversible, *albeit* relatively slow, demethylation to form, **1a**. This can be seen in Fig. 8. When held at pH 11.5 for 2 h a decrease in absorbance at 350 nm is observed and upon acidification to pH 2, the spectrum resembles closely that of H**1a**, with only 20% of the original absorption intensity at *ca.* 550 nm. ^{1}H NMR spectroscopy of **2b** (Fig. 9) was used to confirm demethylation at high pH. The deuteriation of the bipy ligands in **2b** simplifies the aromatic region of the spectrum.

Comparison of the ^{1}H NMR spectrum of **2b** at pD 9.5 and pD 12 with that of **1b** at pD 12, in particular the chemical shift

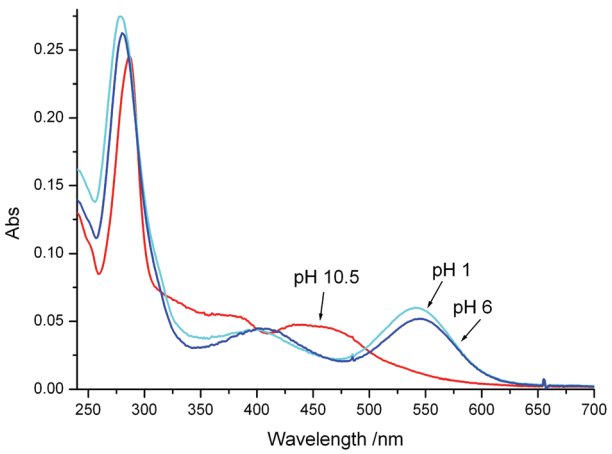

Fig. 7 UV/Vis absorption spectrum of **2a** (5.00×10^{-6} M) at pH 6 followed by increasing the pH to pH 10.5 with NaOH (aq.) and subsequently decreasing the pH to pH 1 with H_2SO_4.

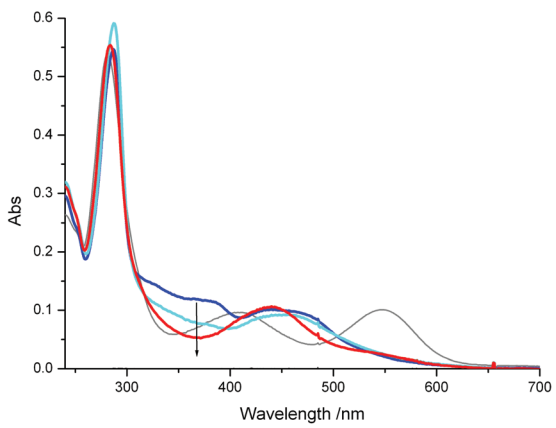

Fig. 8 UV/Vis absorption spectrum of **2a** (1.00×10^{-5} M) at pH 6 (grey line) followed by increasing the pH to pH 11.5 with NaOH (aq.) (dark blue line) and after 2 h (light blue) at pH 11.5 showing the decrease in absorbance at *ca.* 350 nm and subsequent acidification to pH 2 with H_2SO_4 (red line).

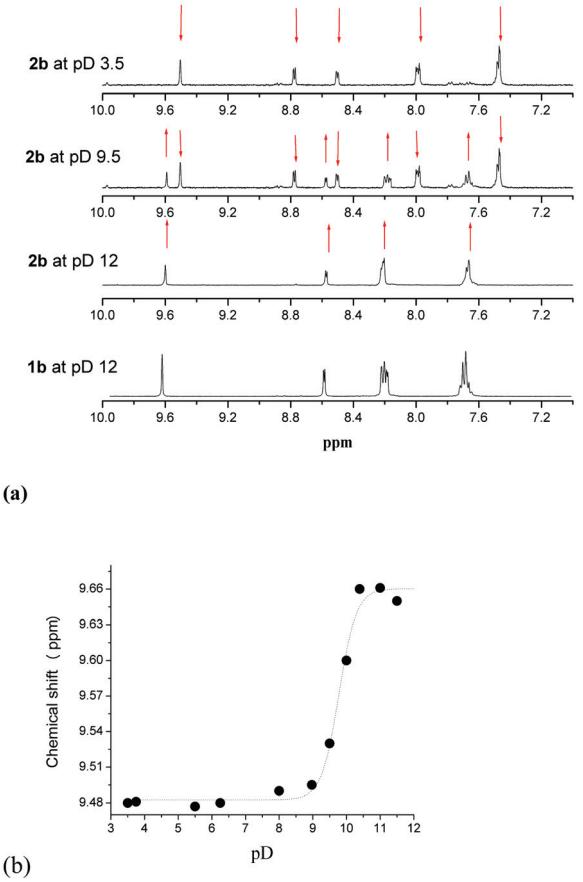

Fig. 9 (a) ^{1}H NMR spectra of **2b** in D_2O at *ca.* pD 3.25, 9.5 and 12 compared with the spectrum of **1b** at pD 12. (b) Plot of chemical shift of pyrazine H3 proton for 2**b** *vs.* pH.

of the H3 hydrogen of the pyrazine ring confirms that demethylation results in reversion of **2b** to **1b**.

Redox properties

The redox processes observed for **2a** are assigned by comparison with those of the precursor **1a**. The Ru(II)/(III) redox couple for **1a** is observed at 0.93 V, and at 1.09 (*vs.* SCE) for its protonated (at the 1,2,4-triazolato ring) form H**1a**.[21] For **2a** the Ru(II)/(III) based oxidation was observed at 1.12 V and, upon protonation to H**2a**, at 1.25 V (*vs.* SCE). The increase in oxidation potential is attributed to the decrease in σ-donor and increase in π-accepter strength of the methylated pyrazine ring compared to a pyrazine ring. As for **1a**, **2a** exhibits several reduction waves at negative potentials. The quasi-reversible redox waves at −1.46 V and −1.72 V for **2a** are equivalent to the bipy based reductions observed for **1a**, however an additional reduction wave at −0.47 V is observed for **2a**, but is not present in the cyclic voltammetry of **1a**. This reduction process is assigned to reduction of the methylated pyrazine ring. The HOMO–LUMO gap calculated for **2a** based on the 1st oxidation and reduction waves is 1.59 eV (780 nm), which is consistent with the lowest energy visible absorption band of **2a**.[28]

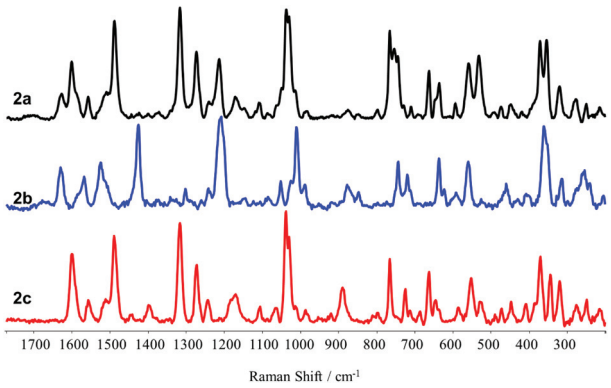

Fig. 10 SERS spectra of **2a–c** on gold colloid at 785 nm.

Surface enhanced and resonance Raman spectroscopy

Although the strong absorption of the complexes in the visible region precluded recording of non-resonant Raman spectra, the surface enhanced Raman spectra (SERS) of **2a–c** could be obtained on colloidal gold at 785 nm and allowed for assignment of the bands of the bipy ligands and the pyrazine ring of the methylated phpztr^{-} ligand (Fig. 10). Raman bands in the SERS spectrum of **2a** at 1625, 1531, 1214, 1051, 746 and 635 cm^{-1} are assigned to the pyrazine moiety and at 1602, 1556, 1488, 1315, 1275, 1172, 1107, 1038, 1028, 767, 752 and 660 cm^{-1} are assigned to the bipy ligands by comparison with the spectra of **2b** and **2c**. The bands assigned to the bipy ligands are as expected compared to related complexes, however in the case of pyrazine based bands direct comparison with the literature is more difficult due to the sensitivity of the pyrazine modes to protonation/substituents on the non-coordinated pyrazine nitrogen.

Resonance Raman (rR) spectroscopy has proven to be an invaluable tool in the assignment of electronic transitions in ruthenium(II) polypyridyl complexes[29–31] and is particularly suited[16,32–35] to complexes in this study where spectra were obtained in CH_3CN at λ_{exc} 355, 400.8, 449, 473, 532 and 561 nm (Fig. 11). Excitation into an allowed Ru → π* transition in mixed ligand complexes gives rise to enhancement of the symmetrical stretching modes of the ligand involved in the transition. In this section the resonance Raman spectroscopy of **2a–c** in all three protonation states is compared with that of **1a**, H**1a** and H_2**1a**.[21]

The excitation wavelength dependence of the ground and excited state rR spectra of **1a–c** were reported previously in all three protonation states (*vide supra*).[21] rR spectra of **1a** at 457.9 nm showed bands attributable to bipy based vibrations at 1610, 1565, 1494, 1429, 1320, 1277 and 1175 cm^{-1}. Only weak bands assigned to modes of the pyrazine ring were observed; at 1534 and 1193 cm^{-1}. The rR spectrum of H**1a** at 457.9 nm showed only bipy based bands. By contrast, the rR spectra of **1a** and H**1a** at 514.5 nm showed relatively weak bands assigned to the bipy ligands and strong pyrazine based bands at 1600, 1529 and 1337 cm^{-1} and 1609, 1517 and 1387 cm^{-1}, respectively.[21] For H_2**1a**, in which the non-coordinated nitrogen

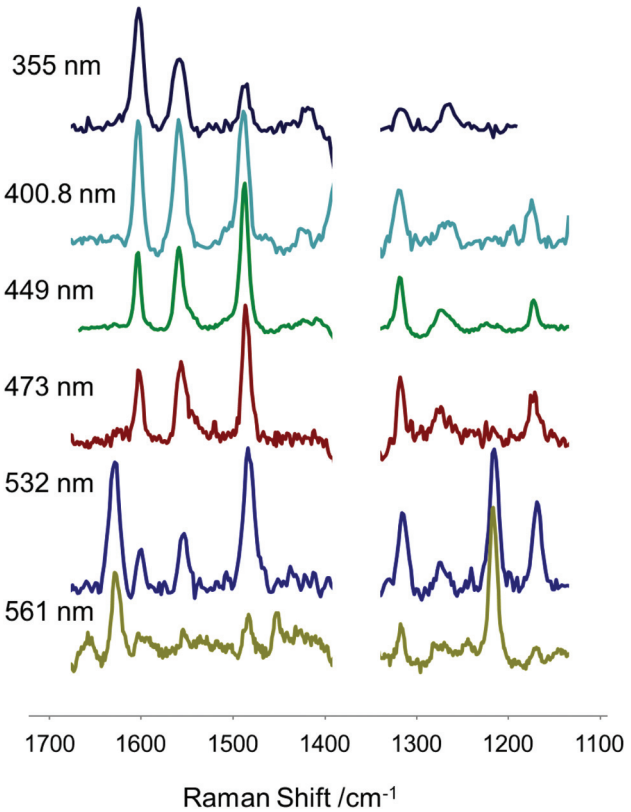

Fig. 11 Resonance Raman spectra of **2a** in CH_3CN recorded at λ_{exc} between 355 and 561 nm.

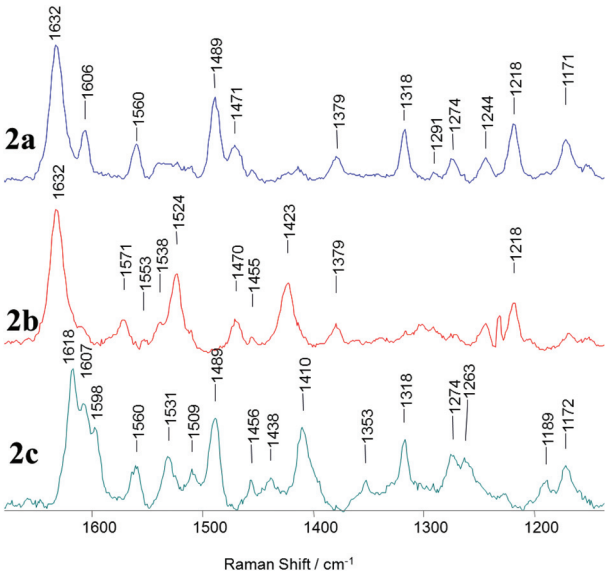

Fig. 12 Resonance Raman spectra of **2a–c** in H_2O, λ_{exc} 488 nm.

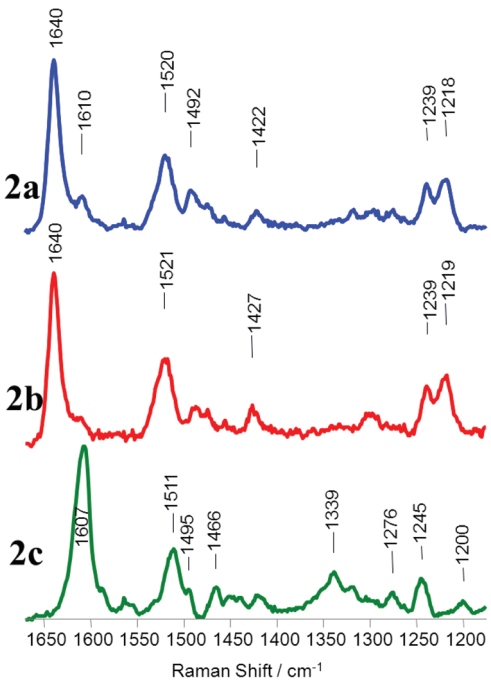

Fig. 13 Resonance Raman spectra of **2a–c** in conc. HCl (aq.), λ_{exc} 488 nm.

of the pyrazine ring is protonated, the rR spectrum at 514.5 nm is dominated by pyrazine based bands at 1633, 1518 and 1474 cm^{-1}, which are most similar to those observed for the pyrazine modes in the SERS spectrum of **2a–c** (*vide supra*).

The rR spectra of **2a** in acetonitrile at various excitation wavelengths is shown in Fig. 11. Notably between 355 nm and 473 nm the Raman spectrum is comprised of bands assignable exclusively to bipy based modes. At 532 and 561 nm the spectrum is dominated by pyrazine based modes, which is confirmed by comparison with the spectra of **1b** and **1c**. The wavelength dependence of the rR spectrum allows for assignment of the longest wavelength absorption band (at *ca.* 550 nm) to pyrazine based ^{1}MLCT ← GS transitions and the absorption band at *ca.* 430 nm to bipy based ^{1}MLCT ← GS transitions (Fig. 15).

The absorption spectra for **2a–c** show solvatochromic behaviour, with the lowest energy absorption undergoing a red shift, and the second lowest energy band undergoing a slight blue shift, on going from acetonitrile to water. These changes hold consequences for the wavelength dependence of the Raman spectra. In water the excitation wavelength 488 nm lies between the two main visible bands and is centred at the main absorption band of **2a–c** at pH > 9 (Fig. 12, *vide supra*). The Raman spectrum in water has bands assignable to both the bipy ligands and the pyrazine moiety consistent with the overlap of the two visible absorption bands at 488 nm (Fig. 12). In conc. HCl (aq.), both absorption bands undergo a blue shift and hence the lowest energy absorption moves into resonance at 488 nm and the shorter wavelength band moves out of resonance (Fig. 13). Under these conditions the spectra are dominated by the bands arising for pyrazine vibrational modes with negligible contributions from bipy modes. At pH > 9 the Raman spectrum is considerably simplified and shows features of the bipy ligands exclusively (Fig. 14).

Although the wavenumbers of the bipy modes are relatively insensitive to either solvent or pH, the pyrazine modes show

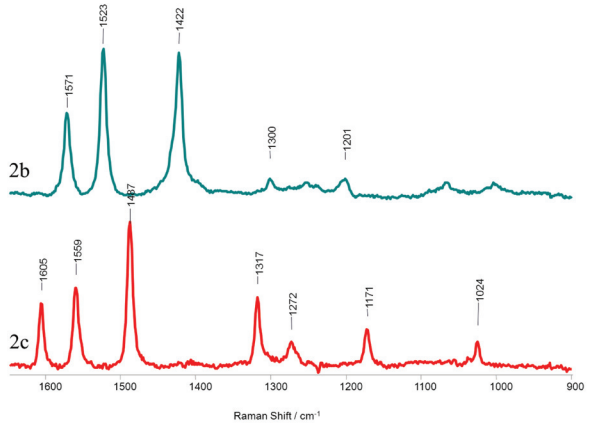

Fig. 14 Resonance Raman spectra of **2b** and **2c** in H_2O at pH 10, λ_{exc} 488 nm.

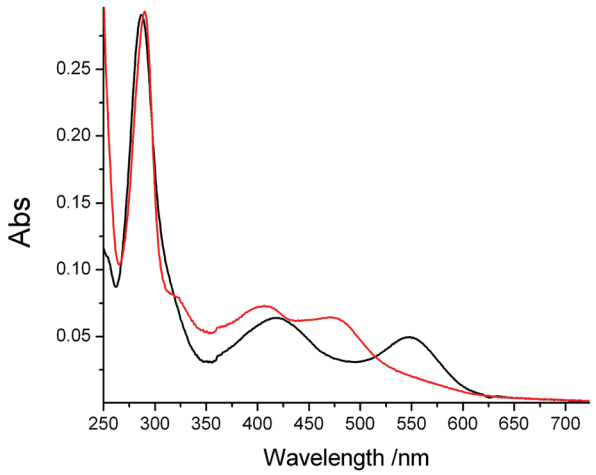

Fig. 15 UV/Vis absorption spectra of **2a** (5.00×10^{-6} M) in CH_3CN (black) and in CH_3CN with Et_3N added to deprotonate the complex (red).

considerable sensitivity. The most prominent band assignable to the pyrazine ring in the rR spectra of **2a** is at around 1625–1632 cm^{-1}, which is comparable with that of H_2**1a** (1633 cm^{-1}) in which the pyrazine ring is protonated (Fig. 12). When the triazolato ring of **2a** is protonated (*i.e.* H**2a**) this band is blue shifted to 1640 cm^{-1} (Fig. 13).

Transient resonance Raman spectroscopy

Although neither of the complexes **2a–c** or their protonated formed H**2a–c** are emissive in acetonitrile solution, deprotonation of the complexes at the methyl group results in substantial changes to the electronic structure of the complexes, not least by raising the LUMO energy of the pyrazine ring above that of the bipy ligands, specifically the absorption band at 550 nm undergoes a substantial blue shift to *ca.* 470 nm (Fig. 15). If a bipy based ^{3}MLCT state is populated to a significant extent then the characteristic features of the bipy anion radical should be observed using transient resonance Raman (TR^2) spectroscopy at λ_{exc} 355 nm.[36] The TR^2 spectra for complexes **2a–c** are shown in Fig. 16. It is clear that the characteristic

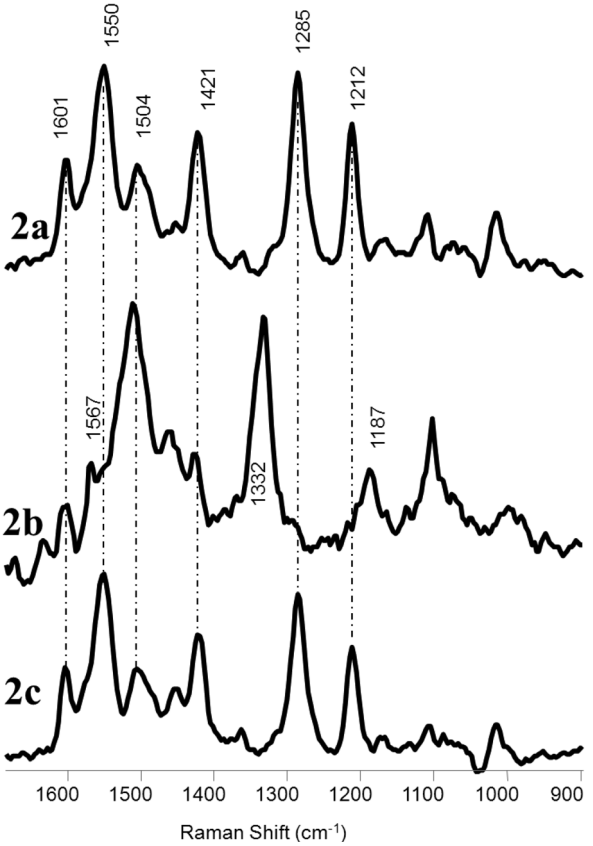

Fig. 16 Transient resonance Raman spectra at λ_{exc} 355 nm of **2a–c** in CH_3CN with Et_3N (solvent subtracted, pulse width 6 ns, 3 mJ, 10 Hz).

[H_8]-bipy anion radical bands at 1285 and 1212 cm^{-1} are observed for **2a** and **2c**, while for **2b** the bands of the [D_8]-bipy anion radical are observed at 1332 and 1187 cm^{-1}.[35] Addition of acid to the deprotonated complexes afterwards results in a complete loss in the bipy radical anion bands and results in a spectrum similar to that obtained for **2a–c** using continuous wave excitation at 355 nm (*vide supra*) indicating that demethylation was not significant on the timescale over which the TR^2 spectroscopic data was acquired.

Conclusions

In the present study the unexpected methylation of the pyrazine ring of **1a–c** to yield **2a–c** is reported. Confirmation of selective pyrazine methylation of **1a** was obtained on the basis of ^{1}H NMR, UV/Vis absorption, emission and (resonance) Raman spectroscopy. This result is in contrast to the related complex $[Ru(bipy)_2(pztr)]^+$ in which the phenyl group of **1a** is replaced by a hydrogen. In the case of $[Ru(bipy)_2(pztr)]^+$ the 1,2,4-triazolato moiety undergoes methylation with a N1/N4 ratio of 70/30 (Fig. 2).[7] The difference in behaviour could be ascribed to the increased steric hindrance provided by the phenyl ring in **1**, which impedes the approach of the $(CH_3)_3O^+$ sufficiently to render pyrazine *N*-methylation competitive.

However, the increased acidity of the contribution from the pyrazine nitrogen in **1a** (pK_a = 3.1)[21] compared to the analogous complex without the phenyl group (pK_a = 3.5) suggests that the change in selectivity is electronic in origin.

The acid–base chemistry of **2a–c** shows that the methyl hydrogens are relatively acidic and undergo deprotonation at pH 9.9. In the deprotonated state the electronic properties of the complexes are similar to those of the non-methylated complexes **1a–c**, where the lowest excited state is a bipy based ^{3}MLCT state. Although the deprotonated complexes are relatively stable, over time basic conditions lead to loss of the methyl group to recover **1a–c**. Hence in addition to methylation being a useful synthetic tool to reversibly modify the electronic properties of the **1a–c**, it is also fully reversible and hence useful as a protection method in the synthesis of heterobinuclear complexes since deprotection is simply carried out by adding base at room temperature. A similar approach was reported by Serroni *et al.* who used DABCO to deprotect the methylated pyrazine groupings.[8]

Experimental

All solvents employed for synthesis were of HPLC grade and for spectroscopy, UVASOL. All reagents employed were of reagent grade or better and used as received. 2-(5′-phenyl-4′H-[1,2,4]-triazol-3′-yl)-pyrazine (Hphpztr),[37] 2-(5′-phenyl-4′H-[1,2,4]triazol-3′-yl)-[D_3]-pyrazine ([D_3]-Hphpztr),[17] *cis*-[Ru(bipy)$_2$Cl$_2$]·2H$_2$O,[38] *cis*-[Ru([D_8]-bipy)$_2$Cl$_2$]·2H$_2$O and [Ru(bipy)$_2$(phpztr)](PF$_6$)·2H$_2$O and its isotopologues (**1a–c**)[36,39] were available from earlier studies and prepared by literature methods.

Synthesis

[Ru(bipy)$_2$(phpztr)](PF$_6$)$_2$ (2a). An excess of Me_3OBF_4 was added to 38.7 mg (0.05 mmol) of [Ru(bipy)$_2$(phpztr)]PF$_6$ (**1a**) and 28 mg (0.21 mmol) of Na_2CO_3 in 10 cm^3 of dry acetonitrile in one portion at room temperature under argon. The resulting purple solution was stirred for 1 h and the solvent was removed *in vacuo*. The residue was dissolved in the minimum amount of water and precipitated with conc. NH_4PF_6 solution and recrystallised from acetone/water (50/50 v/v). Yield 38 mg (0.04 mmol, 82%). ^{1}H NMR in CD_3CN; 9.15 (1H, s, pzH3), 8.55 (4H, m, bipyH3), 8.37 (1H, d, pzH5), 8.01 (4H, m bipyH4), 7.98 (3H, m, pz H6/phH2/H5), 7.89 (1H, d, bipyH6), 7.80 (1H, d, bipyH6), 7.66 (1H, d, bipyH6) 7.58 (1H, d, bipyH6) 7.45 (7H, m, bipyH5 and phH3/H4/H5), 4.25 (3H, s, Me). ESI-MS **2a**$^{2+}$ (calcd $RuC_{33}H_{27}N_9$: 325) found: 325.4 *m*/*z*. Elemental analysis (calcd $RuC_{33}H_{27}N_9P_2F_{12}$) C: 42.1% (41. 9%), H: 2.87% (2.31%), N: 13.40% (13.21%).

[Ru([D_8]-bipy)$_2$(phpztr)](PF$_6$)$_2$ (2b). As for **2a** except an excess of Me_3OBF_4 was added to 35 mg (0.044 mmol) of [Ru([D_8]-bipy)$_2$(phpztr)]PF$_6$ (**1b**) Yield 31.5 mg (0.033 mmol, 76%). ^{1}H NMR in CD_3CN. 9.15 (1H, s, pzH3), 8.36 (1H, d, 3 Hz, pzH5), 7.80 (3H, m, phH2/H5, pzH6), 7.44 (3H, m, phH3/H4/H5), 4.25 (3H, s, Me). ESI-MS **2b**$^{2+}$ (calcd for $RuC_{33}H_{11}N_9D_{16}$: 333) found: 333.4 *m*/*z*. Elemental analysis (calcd for $RuC_{33}H_{11}N_9D_{16}P_2F_{12}$) C: 40.1% (39.2%), H: 2.35% (2.97%), N: 11.86% (12.48%).

[Ru(bipy)$_2$([D_3]-phpztr)]PF$_6$ (2c). As for **2a** except an excess of Me_3OBF_4 was added to 40 mg (0.05 mmol) of [Ru(bipy)$_2$([D_3]-phpztr)]PF$_6$ (**1c**). Yield 39 mg (0.042 mmol, 84%). ^{1}H NMR in CD_3CN. 8.44 (4H, m, bipyH3), 8.01 (4H, m bipyH4), 7.89 (2H, d, phH2/H5), 7.78 (1H, d, bipyH6), 7.69 (1H, d, bipyH6), 7.65 (1H, d, bipyH6) 7.48 (1H, d, bipyH6) 7.44 (7H, m, bipyH5 and phH3/H4/H5), 4.15 (3H, s, Me). ESI-MS **2c**$^{2+}$ (calcd $RuC_{33}H_{24}N_9D_3$: 326.5) found: 326.9 *m*/*z*. Elemental analysis (calcd $RuC_{33}H_{24}N_9D_3$ P_2F_{12}) C: 40.9% (40.5%), H: 2.85% (2.96%), N: 12.52% (12.87%).

Physical measurements

^{1}H NMR (400 MHz, Bruker), UV/Vis absorption (Specord600, AnalyticJena) and emission (JASCO-7200 spectrofluorimeter) spectroscopy, mass spectrometry and electrochemistry (CH-Instruments CH600B potentiostat, GC working electrode, Pt counter electrode and SCE reference electrode),[40] resonance Raman,[41] and transient resonance Raman (TR^2),[42] were carried out as reported previously.

SERS spectra were recorded at λ_{exc} 785 nm using a Perkin Elmer Raman Station at room temperature. Raman spectra were obtained with excitation at 400.8 (50 mW at source, PowerTechnology), 449 nm (35 mW at source, PowerTechnology), 473 (100 mW at source, Cobolt Lasers), 532 nm (300 mW at source, Cobolt Lasers), 561 nm (100 mW at source, Cobolt Lasers), at 457.9/514.5/488 nm (10–50 mW, Spectra Physics Argon Laser) and 355 nm (10 mW, Cobolt Lasers) to the sample through a 5 cm diameter plano-convex lens (f = 6 cm) and Raman scattering collected and collimated in a 180° back-scattering arrangement and focused by a second 5 cm diameter plano convex lens (f = 6 cm) through a long pass edge filter (Semrock) into a Shamrock300i spectrograph (Andor Technology) with a 1200 line mm^{-1} grating blazed at 500 nm, or 2400 line mm^{-1} blazed at 400 nm and acquired with an DV420 CCD camera (Andor Technology). The spectral slit width was set to 10 or 20 μm. Each spectrum was accumulated, typically 10–20 times with 1–5 s acquisition time. Data were recorded and processed using Solis (Andor Technology) with spectral calibration performed using the Raman spectrum of acetonitrile–toluene 50 : 50 (v : v). Samples were 0.1 mM and held in quartz 10 mm path length cuvettes. Transient resonance Raman spectra were recorded using the same system but with excitation with the output of a frequency tripled Innolas Spitlight200 Nd-Yag laser operating at 10 Hz. The leading edge of the pulse excited the sample with the trailing edge probing the excited state formed. The UV/Vis absorption spectra were recorded before and after each Raman measurement to verify that no change had taken place during the measurement. Baseline correction was performed for all spectra.

Elemental analysis was carried out at the Micro-analytical Laboratory at University College Dublin. The pH dependence of the absorption spectra of **1a** was monitored in Britton–Robinson buffer. pH adjustments were made by adding 1 M NaOH or 1 M H_2SO_4 to a 100 cm^3 volume of the dissolved complex.

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